Biosensors and Bioelectronics 77 (2016) 871–878

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Luminescent silica nanoparticles for sensing acetylcholinesterase-catalyzed hydrolysis of acetylcholine

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ARTICLE INFO

Article history:
Received 20 August 2015
Received in revised form
1 October 2015
Accepted 20 October 2015
Available online 22 October 2015

Keywords:
Acetylcholinesterase
Acetylcholine
Enzymatic hydrolysis
Silica nanoparticles
Luminescence
Tb(III) complex

ABSTRACT

This work highlights the H-function of Tb(III)-doped silica nanoparticles in aqueous solutions of acetic acid as a route to sense acetylcholinesterase-catalyzed hydrolysis of acetylcholine (ACh). The H-function results from H^+-induced quenching of Tb(III)-centered luminescence due to protonation of Tb(III) complexes located close to silica/water interface. The H-function can be turned on/switched off by the concentration of complexes within core or nanoparticle shell zones, by the silica surface decoration and adsorption of both organic and inorganic cations on silica surface. Results indicate the optimal synthetic procedure for making nanoparticles capable of sensing acetic acid produced by enzymatic hydrolysis of acetylcholine. The H-function of nanoparticles was determined at various concentrations of ACh and AChE. The measurements show experimental conditions for fitting the H-function to Michaelis–Menten kinetics. Results confirm that reliable fluorescent monitoring AChE-catalyzed hydrolysis of ACh is possible through the H-function properties of Tb(III)-doped silica nanoparticles.

1. Introduction

Luminescent silica nanoparticles have gained great attention during recent decades due to their applications in bioanalysis (Genovese et al., 2014; Wang et al., 2014). Sensing function of these nanoparticles is based on their interactions with substrates, followed by a fluorescent response of luminophores doped into silica nanoparticles. Thus both binding/adsorption capacities of silica/water interface and accessibility of luminophores for interactions with substrates are of great interest for novel analytical applications of the sensing function of luminescent nanoparticles.

Lanthanide complexes as luminophores for doping silica nanoparticles provide new opportunities for sensing function compared to organic luminophores. These opportunities result from photophysical characteristics of lanthanide-centered luminescence (Li and Yan, 2014; Lin et al., 2015), which enables to get both good signal-to-noise ratio even in the presence of background luminescence of proteins, and a switching of lanthanide-centered luminescence by substrates (Chen et al., 2015). The substrate-induced switching of a lanthanide-centered luminescence is the basis for numerous lanthanide-based assays (Chen et al., 2015; Bünzli and Piguet, 2005), including sensing of enzyme activity (Lipchik and Parker, 2013; Duportail et al., 1980; Doughan et al., 2014; Terai et al., 2006; Giardiello and Lowe, 2009). It is worth noting that sensing abilities of lanthanide complexes in solutions and those encapsulated into silica nanoparticles are different. Indeed, interactions of lanthanide complexes with substrates are greatly affected by both silica/water interface and silica surface decoration (Comby et al., 2014; Davydov et al., 2012; Mukhametshina et al., 2014, 2015a, 2015b; Bochkova et al., 2012; Pihlasalo et al., 2012).

Nanoparticles with H-function capable of sensing pH both in vitro and in vivo are of great importance for monitoring proton release during biochemical processes (Sun et al., 2011). Main factors guiding the H-function of lanthanide-doped silica nanoparticles are the subject of the present report. In particular, both silica surface decoration and modification of doping procedure were investigated in order to optimize the optimal synthetic strategy for workable H-function.

Hydrolysis of acetylcholine releases choline and acetic acid (Scheme 1). Thus, the H-function of lanthanide-doped silica nanoparticles may sense acetic acid coming from hydrolysis of acetylcholine (ACh) catalyzed by acetylcholinesterase (AChE). The activity of AChE gains great attention due to the crucial role of this enzyme in living systems (Sauvaître et al., 2007; Tsai and Doong, 2005; Aynacıa et al., 2014; Dhull et al., 2013; Hoskovcová and

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http://dx.doi.org/10.1016/j.bios.2015.10.059
0956-5663/